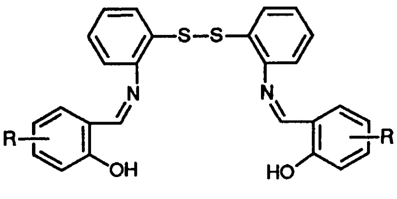
Synthesis of Nickel(II), Copper(II), Zinc(II), and Cadmium(II) Complexes of 2-[(2-Mercaptophenyl)iminomethyl]pyrrole and 2-[(2-Mercaptoethyl)-iminomethyl]pyrrole by the Electrochemical Cleavage of a Disulphide Bond: the Crystal Structure of Bis{2-[(pyrrol-2-yl)methyleneamino]thiophenolato-*S,N*}zinc(II)†

Jesus Castro, Jaime Romero, José A. García-Vázquez, María L. Durán, Alfonso Castiñeiras, and Antonio Sousa*
Departamento de Química Inorgánica, Universidad de Santiago, Santiago de Compostela, Spain
David E. Fenton
Department of Chemistry, The University, Sheffield S3 7HF

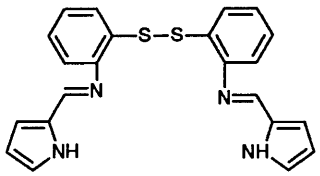
The electrochemical oxidation of anodic metal (nickel, copper, zinc, or cadmium) in acetonitrile solutions of the Schiff bases derived from 2-pyrrolecarbaldehyde and bis(2-aminophenyl)disulphide (H_2L_2) or cysteamine ($H_2L'_2$) gives compounds [ML], [ML′] or [Zn(HL)$_2$]. The crystal structure of bis{2-[(pyrrol-2-yl)methyleneamino]thiophenolato}zinc(II) is orthorhombic, space group *Pbca* with $a = 13.764(3)$, $b = 17.819(1)$, $c = 16.593(2)$ Å, and $Z = 8$. The zinc atom has ZnS_2N_2 distorted tetrahedral stereochemistry and the pyrrolic nitrogen atoms are not co-ordinated.

The presence of anionic sulphur atoms, from cysteine, in a number of DNA and RNA binding proteins has stimulated interest in the synthesis of zinc complexes from ligands bearing sulphur atoms.[1] Copper(II)–cysteine thiolato interactions have also attracted considerable interest because they are present in the low symmetry Type I copper sites of 'blue' copper proteins such as azurin and plastocyanin.[2] The presence of a distorted tetrahedral N_2SS' co-ordination around copper(II) in these proteins has produced a wealth of studies on copper(II) complexes of mixed N and S donor ligands, such as Schiff bases, as models for these proteins.[3] The synthetic problems in the development of these model complexes are associated with the difficulty of preparing the free Schiff bases[4] and with the instability of the copper(II)–thiolato bond with respect to copper(I) and disulphide.[5]

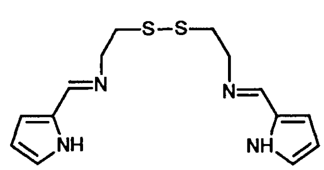
Recently we have shown that these difficulties may be overcome by making use of an electrochemical reductive cleavage of the disulphide bond present in preformed Schiff bases such as (1)—(3).[6] Following a similar procedure we report here the synthesis of nickel(II), copper(II), zinc(II), and cadmium(II) complexes of 2-[(2-mercaptophenyl)iminomethyl]pyrrole and 2-[(2-mercaptoethyl)iminomethyl]pyrrole produced by cleavage of Schiff bases H_2L_2 (2) and $H_2L'_2$ (3). The crystal structure of [Zn(HL)$_2$] is also reported.



(1)



(2)



(3)

Experimental

Microanalyses were determined on a Perkin-Elmer 240B microanalyser and the analytical data are given in Table 1. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 180 spectrophotometer. The optical spectra were recorded on a Beckman DK-2 diffuse reflectance spectrophotometer and ^1H n.m.r. spectra on a Bruker WM 250 MHz spectrometer. The magnetic data were recorded using a SQUID.

Syntheses.—Acetonitrile, 2-pyrrolecarbaldehyde, bis(2-aminophenyl)disulphide and cysteamine dihydrochloride were used as supplied. The metals (Ega Chemie) were used as plates (*ca.* 2 × 2 cm).

Schiff base formation. Cysteamine dihydrochloride (2 mmol) was suspended in absolute ethanol (20 cm^3) and treated with methanolic NaOH (4 cm^3, 1 mol dm^{-3}) with stirring. The reaction mixture was stirred at room temperature for *ca.* 5 h and the solvent was then evaporated *in vacuo* and replaced by benzene (20 cm^3) prior to Schiff base formation. Addition of a solution of the aldehyde (2 mmol) in benzene (30 cm^3) with

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

stirring to a solution of the cysteamine as prepared above gave a clear solution which was refluxed until the theoretical amount of water was collected in a Dean–Stark trap. Evaporation of solvent *in vacuo* gave an oil which was stirred with CCl_4 to produce a brown powdery solid.

The Schiff base derived from bis(2-aminophenyl) disulphide was prepared by a method similar to the one described above but using $CHCl_3$ as the solvent. After concentration the oil obtained was stirred with hexane to give a cream solid. The purity of both Schiff bases was checked by i.r. and ^1H n.m.r. spectroscopies prior to use in the electrochemical syntheses.

Electrochemical Syntheses.—The electrochemical method used in the synthesis of the metal complexes is similar to that described by Tuck and co-workers.[7] The cell was a tall-form beaker (100 cm^3); a metal foil formed the anode, and a platinum wire the cathode. The ligand was dissolved in acetonitrile (*ca.* 50 cm^3) and tetramethylammonium perchlorate (*ca.* 10 mg) was added to the solution as the supporting electrolyte. The cell can be summarized as $Pt(-)|MeCN + H_2L_2|M(+)$. As the electrolysis proceeded, hydrogen gas was evolved at the cathode, and the formation of an insoluble compound was generally observed within a few minutes. The precipitate was collected, washed with acetonitrile and diethyl ether, dried *in vacuo* and identified as [ML] or [ML′]. The remaining solution phase was concentrated at room temperature and in the case of the base H_2L_2 with zinc as the anode a microcrystalline precipitate of composition $Zn(HL)_2$ was isolated and recrystallized from acetonitrile to give yellow air-stable crystals suitable for *X*-ray studies. We were not able to recover any identifiable compounds from the solution phase of the other experiments. Details of solution composition and electrochemical conditions are given in Table 2.

Crystal Structure Determination of $[Zn(HL)_2]$.—*Crystal data.* $C_{22}H_{18}N_4S_2Zn$, $M = 467.90$, orthorhombic, space group *Pbca*, $a = 13.764(3)$, $b = 17.819(1)$, $c = 16.593(2)$ Å, $U = 4\,069.6(2)$ Å^3, $Z = 8$, $D_c = 1.521$ g cm^{-3}, $F(000) = 1\,904$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,73$ Å, $\mu(\text{Mo-}K_\alpha) = 14.476$ cm^{-1}.

A prismatic crystal (dimensions 0.16 × 0.12 × 0.32 mm) was used for the data collection on a CAD4 automated four-circle diffractometer at room temperature, by the ω—θ scan technique with graphite-monochromated Mo-K_α radiation. 6 992 Intensities registered to $\theta_{max.}$ 25°, 3 126 unique reflections ($R_{int.}$ 0.027) of which 1 406 with $I > 3\sigma(I)$ were used in the refinement. They were corrected for Lorentz-polarization factors; an empirical absorption correction[8] was applied (minimum and maximum transmission values 0.847, 1.206).

The structure was solved by direct methods and was refined by full-matrix least squares. All non-hydrogen atoms were assigned anisotropic thermal parameters, and the hydrogen atoms were included in structure factor calculations with $B_{iso} = 4.0$ Å^2 fixed, but not refined. The weighting scheme used was $w^{-1} = \sigma^2(F_o)$. The agreement factor converged to $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.033$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.034$, and $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}} = 2.428$ for 263 variables (N_o = number of observations, N_v = number of variables). The largest shift/e.s.d. in the final least-squares cycle was 0.001; the maximum residual electron density in the Fourier difference map was 0.290 e Å^{-3}; the secondary extinction coefficient was 4.4153×10^{-8}.[9] Neutral scattering factors were taken from ref. 10. Computations were performed on a DEC MicroVAX II computer by using SHELXS[11] and SDP/VAX.[12]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 1. Analytical data (%)* for the complexes

Compound	C	N	H
[NiL]	50.5 (51.0)	10.7 (10.8)	3.4 (3.1)
[CuL]	49.8 (50.1)	10.5 (10.6)	3.1 (3.0)
[ZnL]	49.5 (49.7)	10.2 (10.5)	3.1 (3.0)
$[Zn(HL)_2]$	56.6 (56.5)	11.9 (12.0)	3.9 (3.9)
[CdL]	42.7 (42.3)	9.2 (9.0)	2.8 (2.6)
[NiL′]	39.6 (39.9)	13.6 (13.3)	3.7 (3.8)
[CuL′]	39.1 (39.0)	12.7 (13.0)	3.6 (3.7)
$[ZnL']\cdot H_2O$	36.3 (35.7)	12.2 (11.9)	4.3 (4.3)
$[CdL']\cdot 2H_2O$	28.3 (28.0)	9.2 (9.3)	4.1 (4.0)

* Calculated values given in parentheses.

Results and Discussion

The studies described above show that an electrochemical reductive cleavage of the disulphide bond present in the preformed Schiff bases, H_2L_2 or $H_2L'_2$, can be used to obtain complexes [ML] or [ML′] (M = Ni, Cu, Zn, or Cd), which are otherwise difficult to prepare by conventional synthetic routes.[13] For the base H_2L_2 the compound $[Zn(HL)_2]$ was obtained together with the complex [ZnL].

The electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, E_F, was found to be about 0.5 mol F^{-1} for nickel, zinc, and cadmium (see Table 2). The reaction mechanism can therefore be written as equations (1) and (2) for the [ML] and $[Zn(HL)_2]$ systems respectively.

$$\text{Cathode: } \tfrac{1}{2}H_2L_2 + 2e^- \longrightarrow L^{2-} + \tfrac{1}{2}H_2(g)$$
$$\text{Anode: } L^{2-} + M \longrightarrow [ML] + 2e^- \quad (1)$$

$$\text{Cathode: } H_2L_2 + 2e^- \longrightarrow 2HL^-$$
$$\text{Anode: } 2HL^- + Zn \longrightarrow [Zn(HL)_2] + 2e^- \quad (2)$$

Table 2. Experimental conditions for the electrochemical syntheses

Metal	Ligand	Amount of ligand[a] (g)	Initial voltage[b] (V)	Time (h)	Metal dissolved (mg)	E_F/ mol F^{-1}
Ni	H_2L_2	0.24	30	3	67	0.51
Cu	H_2L_2	0.23	30	1.5	71	0.99
Zu	H_2L_2	0.23	19	1.5	38	0.52
Cd	H_2L_2	0.16	15	2	86	0.51
Ni	$H_2L'_2$	0.28	25	1	23	0.52
Cu	$H_2L'_2$	0.30	25	1	51	1.1
Zn	$H_2L'_2$	0.23	15	2	48	0.49
Cd	$H_2L'_2$	0.23	28	2	82	0.49

[a] Plus NMe_4ClO_4 (*ca.* 10 mg). [b] Voltage required to produce a current of 20 mA.

Table 3. Final atomic co-ordinates for $[Zn(HL)_2]$

Atom	*X/a*	*Y/b*	*Z/c*
Zn	0.212 32(5)	0.452 28(4)	0.229 57(4)
S(1)	0.1872(1)	0.3277(1)	0.2129(1)
S(21)	0.1674(1)	0.5530(1)	0.1555(1)
N(1)	0.1419(3)	0.4444(3)	0.3393(3)
N(2)	0.2332(5)	0.5981(3)	0.3589(4)
N(21)	0.3510(4)	0.4934(2)	0.2355(3)
N(22)	0.3597(4)	0.3611(3)	0.3490(3)
C(1)	0.0911(4)	0.3257(3)	0.2827(4)
C(2)	0.0257(5)	0.2654(4)	0.2828(4)
C(3)	−0.0512(5)	0.2632(4)	0.3350(5)
C(4)	−0.0666(5)	0.3205(4)	0.3884(5)
C(5)	−0.0038(5)	0.3798(4)	0.3916(4)
C(6)	0.0760(5)	0.3826(3)	0.3400(4)
C(7)	0.1626(5)	0.4754(3)	0.4075(4)
C(8)	0.2159(5)	0.5438(4)	0.4162(3)
C(9)	0.2575(5)	0.5673(3)	0.4883(4)
C(10)	0.2985(7)	0.6332(5)	0.4744(5)
C(11)	0.2880(6)	0.6541(4)	0.3987(5)
C(21)	0.2865(4)	0.5851(3)	0.1411(3)
C(22)	0.3024(5)	0.6443(4)	0.0872(4)
C(23)	0.3943(5)	0.6695(4)	0.0718(4)
C(24)	0.4736(5)	0.6366(4)	0.1077(4)
C(25)	0.4600(5)	0.5784(3)	0.1620(4)
C(26)	0.3670(4)	0.5536(3)	0.1801(3)
C(27)	0.4132(5)	0.4847(3)	0.2944(4)
C(28)	0.4142(4)	0.4256(3)	0.3508(4)
C(29)	0.4688(5)	0.4225(4)	0.4212(4)
C(210)	0.4465(5)	0.3558(4)	0.4592(4)
C(211)	0.3807(5)	0.3197(4)	0.4148(4)

Table 4. Bond distances (Å) and angles (°) for $[Zn(HL)_2]$

Zn–S(1)	2.265(1)	C(3)–C(4)	1.367(7)
Zn–S(21)	2.262(1)	C(4)–C(5)	1.366(6)
Zn–N(1)	2.067(3)	C(5)–C(6)	1.395(7)
Zn–N(21)	2.047(3)	C(7)–C(8)	1.430(6)
S(1)–C(1)	1.758(4)	C(8)–C(9)	1.391(6)
S(21)–C(21)	1.753(4)	C(9)–C(10)	1.324(7)
N(1)–C(6)	1.426(5)	C(10)–C(11)	1.318(8)
N(1)–C(7)	1.291(5)	C(21)–C(22)	1.400(6)
N(2)–C(8)	1.378(5)	C(21)–C(26)	1.400(5)
N(2)–C(11)	1.414(7)	C(22)–C(23)	1.368(7)
N(21)–C(26)	1.430(5)	C(23)–C(24)	1.374(6)
N(21)–C(27)	1.310(5)	C(24)–C(25)	1.387(6)
N(22)–C(28)	1.373(5)	C(25)–C(26)	1.388(6)
N(22)–C(211)	1.349(6)	C(27)–C(28)	1.408(6)
C(1)–C(2)	1.401(6)	C(28)–C(29)	1.390(6)
C(1)–C(6)	1.406(6)	C(29)–C(210)	1.380(6)
C(2)–C(3)	1.369(7)	C(210)–C(211)	1.332(7)
S(1)–Zn–S(21)	132.08(5)	N(2)–C(8)–C(9)	108.2(5)
S(1)–Zn–N(1)	88.3(1)	C(7)–C(8)–C(9)	123.7(5)
S(1)–Zn–N(21)	119.94(9)	C(8)–C(9)–C(10)	107.0(5)
S(21)–Zn–N(1)	113.9(1)	C(9)–C(10)–C(11)	111.7(5)
S(21)–Zn–N(21)	89.8(1)	N(2)–C(11)–C(10)	107.8(5)
N(1)–Zn–N(21)	114.9(1)	S(21)–C(21)–C(22)	118.6(3)
C(6)–N(1)–C(7)	117.7(4)	S(21)–C(21)–C(26)	123.1(3)
C(8)–N(2)–C(11)	105.4(4)	C(22)–C(21)–C(26)	118.4(5)
C(26)–N(21)–C(27)	117.9(3)	C(21)–C(22)–C(23)	120.8(4)
C(28)–N(22)–C(211)	108.9(5)	C(22)–C(23)–C(24)	121.0(4)
S(1)–C(1)–C(2)	119.9(4)	C(23)–C(24)–C(25)	119.6(4)
S(1)–C(1)–C(6)	122.8(3)	C(24)–C(25)–C(26)	120.3(4)
C(2)–C(1)–C(6)	117.2(4)	N(21)–C(26)–C(21)	118.5(3)
C(1)–C(2)–C(3)	121.3(5)	N(21)–C(26)–C(25)	121.4(4)
C(2)–C(3)–C(4)	120.6(5)	C(21)–C(26)–C(25)	120.1(4)
C(3)–C(4)–C(5)	120.3(5)	N(21)–C(27)–C(28)	126.3(4)
C(4)–C(5)–C(6)	120.2(5)	N(22)–C(28)–C(27)	127.3(4)
N(1)–C(6)–C(1)	117.3(4)	N(22)–C(28)–C(29)	106.2(4)
N(1)–C(6)–C(5)	122.3(4)	C(27)–C(28)–C(29)	126.5(5)
C(1)–C(6)–C(5)	120.4(4)	C(28)–C(29)–C(210)	107.3(5)
N(1)–C(7)–C(8)	124.5(4)	C(29)–C(210)–C(211)	108.3(5)
N(2)–C(8)–C(7)	128.2(4)	N(22)–C(211)–C(210)	109.2(5)

For the copper complexes, the E_F values are close to 1.0 mol F^{-1}. It can be reasonably postulated that the formation of Cu^I at the anode is followed by oxidation to Cu^{II} in the solution. Such oxidation steps have been observed in other electrochemical syntheses.[14]

Attempts have been made to prepare mixed complexes *via* the electrochemical technique by adding other ligands such as pyridine, 1,10-phenanthroline, or 2,2′-bipyridine to the Schiff-base solution. Unfortunately, such experiments were unsuccessful as the analytical data showed that the isolated compounds still had the general formula [ML] or [ML′]. This contrasts with results obtained in the synthesis of mercaptosalicylaldiminates of copper[6] where it has been possible to prepare mixed complexes of these ligands *via* electrochemical processes.

Description of the Structure of $[Zn(HL)_2]$.—The structure consists of monomeric $[Zn(HL)_2]$ units as shown in the Figure. Final atomic co-ordinates, bond lengths and angles are shown in Tables 3 and 4. The central zinc atom is four-co-ordinated to the sulphur and to the imine nitrogen atoms of two HL^- bidentate ligands. The geometry about the zinc atom is best described as distorted tetrahedral. The average Zn–N(1, 21) bond length of 2.057(3) Å is similar to those found in bis(*N*-butylsalicylaldiminato)zinc(II)[15] and bis[*N*-(4-methylphenyl)-salicylaldiminato]zinc(II),[16] in which there is also distorted tetrahedral geometry about the metal atom. The mean Zn–S distance, 2.263(1) Å, is close to that reported for the Zn–S(terminal) bonds, 2.286(6) Å, in the $[Zn_4(SC_6H_5)_{10}]^{2-}$ anion,[17] which has tetrahedrally co-ordinated zinc. The C–N bond length is in agreement with the value of 1.30 Å proposed for a C=N bond.[18] The pyrrolic nitrogen atoms are not co-ordinated to the zinc.

The infrared spectrum of the complex, Table 5, is consistent with the structural data presented above. The spectrum shows bands attributable to ν(NH) from the non-co-ordinated pyrrole, and the band assignable to the ν(C=N) of the azomethine group undergoes a shift to lower frequency in the complex. This indicates that the azomethine nitrogen is involved in the co-ordination to the zinc.[19] The ^1H n.m.r. data reinforce this conclusion.[20] The spectra of the free ligand and the complex show a peak at δ 11.7 assignable to the hydrogens of the NH groups. The peak of the azomethine hydrogen undergoes a downfield shift in the complex.

[ML] *and* [ML′] *Complexes*.—The i.r. spectra of the complexes [ML] and [ML′] show no bands assignable to ν(NH), indicating that the pyrrolic hydrogen atom is lost during the electrochemical synthesis. In addition, the band attributable to ν(C=N) of the azomethine group is shifted by 15—20 cm^{-1} to lower frequencies in all the metal complexes. This indicates that co-ordination has taken place through the pyrrolic and azomethine nitrogen atoms.[19] For zinc and cadmium complexes, the ^1H n.m.r. data (Table 6) reinforce the above conclusion.[20] Thus, the peak assignable to the hydrogen of the NH group is absent in the spectra of the complexes and the signal of the azomethine hydrogen is shifted downfield.

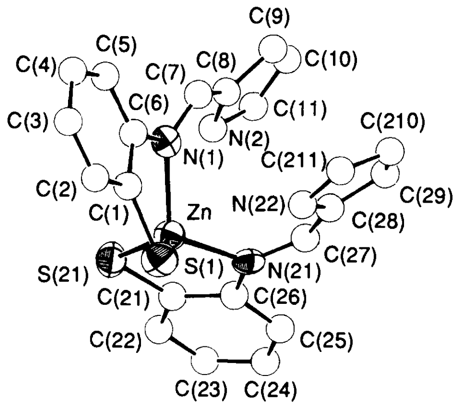


Figure. The molecular structure of bis{2-[(pyrrol-2-yl)methyleneamino]thiophenolato}zinc(II)

Table 5. Important i.r. bands (cm^{-1}) of Schiff bases and their metal complexes

Compound	ν(C=N)	ν(NH)
H_2L_2	1 650	3 310, 3 405
[NiL]	1 575	
[CuL]	1 580	
[ZnL]	1 590	
$[Zn(HL)_2]$	1 605	3 300—3 200
[CdL]	1 595	
$H_2L'_2$	1 645	3 180
[NiL′]	1 600	
[CuL′]	1 590	
[ZnL′]	1 590	
[CdL′]	1 600	

Table 6. Proton n.m.r. chemical shifts (δ) for free ligands, and for their zinc and cadmium complexes

Compound	NH	CH=N
H_2L_2	11.7	8.2
[ZnL]		8.3
$[Zn(HL)_2]$	11.7	8.3
[CdL]		8.5
$H_2L'_2$	11.4	8.1
[ZnL′]		8.3
[CdL′]		8.2

These results show that the ligands behave in a terdentate manner binding to the metals through the pyrrolic nitrogen, the sulphur, and the azomethine nitrogen. On this basis, it is not unreasonable to propose that the [ML] and [ML′] complexes are at least dimeric and possibly polymeric in the solid state as a consequence of the metal atoms in the monomer unit being co-ordinatively unsaturated in the three-co-ordinate environment provided by the terdentate ligand.

The effective magnetic moments, $\mu_{eff.}$, at room temperature, 2.45 for [NiL] and 3.09 for [NiL′], are not compatible with a square-planar co-ordination around the nickel(II) centre. This interpretation is supported by the electronic spectra as the solid-state reflectance spectra of the nickel(II) complexes are very different to those found for the square-planar mercaptosalicylaldiminates of nickel(II).[21] They show two *d–d* bands at *ca.* 8 000 and 12 500 cm^{-1}, which are well within the range for six-co-ordinated octahedral complexes of nickel(II),[22] {[NiL], 7 690 and 12 120; [NiL′], 8 000 and 12 500 cm^{-1}}, and can be assigned to the $^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ transitions, respectively. Therefore a six-co-ordinated polymeric structure is tentatively assigned to the nickel(II) complexes.

The diffuse reflectance spectra of the copper(II) complexes exhibit one very broad unresolved band in the visible region {[CuL], 13 300—22 200; [CuL′], 14 300—22 200 cm^{-1}} and the effective magnetic moments, $\mu_{eff.}$ at room temperature of these complexes are 1.73 for [CuL] and 1.34 for [CuL′]. On the basis of these data, it is very difficult to propose unambiguous structures for these complexes, particularly as the electronic spectra of copper(II) complexes with multidentate ligands are not, in general, good indicators of geometry. Oligomeric structures are likely however in order to alleviate co-ordinative unsaturation at the copper(II) ion.

Acknowledgements

We thank the British Council for support.

References

1 D. T. Corwin, jun., E. S. Gruff, and S. A. Koch, *Inorg. Chim. Acta*, 1988, **151**, 5 and refs. therein.
2 H. C. Freeman, in 'Coordination Chemistry-21,' ed. J. P. Laurent, Pergamon, New York, 1980, p. 29.
3 L. Casella, *Inorg. Chem.*, 1984, **23**, 2781; L. Casella, M. Gullotti, and R. Vigano, *Inorg. Chim. Acta*, 1986, **124**, 121.
4 R. G. Charles and H. Freiser, *J. Org. Chem.*, 1953, **18**, 422.
5 R. C. Coombes, J. P. Costes, and D. E. Fenton, *Inorg. Chim. Acta*, 1983, **77**, L173; H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull. Jpn.*, 1960, **8**, 1012; J. M. Downes, J. Whelan, and B. Bosnich, *Inorg. Chem.*, 1981, **20**, 1081; P. Kroneck, *J. Am. Chem. Soc.*, 1975, **97**, 3839.
6 R. Bastida, M. R. Bermejo, M. S. Louro, J. Romero, A. Sousa, and D. E. Fenton, *Inorg. Chim. Acta*, 1988, **145**, 167.
7 J. J. Habeeb, D. G. Tuck, and F. H. Walters, *J. Coord. Chem.*, 1978, **8**, 27.
8 N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, 1983, **39**, 158.
9 W. H. Zachariasen, *Acta Crystallogr.*, 1963, **16**, 1139.
10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2A (Present distributor D. Reidel, Dordrecht).
11 G. M. Sheldrick, SHELXS 86 Program for the Solution of Crystal Structures from Diffraction Data, University of Göttingen, 1986.
12 B. A. Frenz, in 'Computing Crystallography', Delft, University Press, Delft, 1978; VAXSDP, 1985, Version 2.2, pp. 64—71.
13 H. Jadamus, Q. Fernando, and H. Fresier, *J. Am. Chem. Soc.*, 1964, **86**, 3056.
14 N. M. Atherton, D. E. Fenton, G. J. Hewson, C. H. McLean, R. Bastida, J. Romero, A. Sousa, and E. E. Castellano, *J. Chem. Soc., Dalton Trans.*, 1988, 1059; C. Geloso, R. Kumar, J. Romero, and D. G. Tuck, *Can J. Chem.*, 1987, **65**, 928.
15 E. Frasson and C. Panattoni, *Z. Kristallogr.*, 1961, **116**, 154.
16 T. Sogo, J. Romero, A. Sousa, A. de Blas, M. L. Durán, and E. E. Castellano, *Z. Naturforsch., Teil B*, 1988, **43**, 611.
17 L. Hencher, M. A. Khan, F. F. Said, and D. G. Tuck, *Polyhedron*, 1985, **4**, 1263.
18 J. N. Brown, R. L. Towns, and L. M. Trefonas, *J. Am. Chem. Soc.*, 1972, **92**, 7436.
19 G. C. Percy and D. A. Thornton, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3357.
20 K. Yeh and R. H. Barker, *Inorg. Chem.*, 1967, **6**, 830.
21 G. R. Brubaker, J. C. Latta, and D. C. Aquino, *Inorg. Chem.*, 1970, **9**, 2608.
22 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., Elsevier, Amsterdam, 1984.

Received 12*th March* 1990; *Paper* 0/01075H